PROPERTIES OF ORDINARY PORTLAND CEMENT CLINKER WITH MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH AS RAW MEAL ADDITIVE

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Abstract

Around 1.3 billion tonnes of municipal solid wastes are generated all around the world and out of that around 10% is incinerated generating huge amounts of incineration residues [1]. In Belgium, around 400kT of bottom ash is generated, out of which only 102kT is utilised, mainly as aggregate and road subbase material [2]. Most of the unutilised fraction belongs to the 0-2 mm size fraction. Its utilisation is limited by the presence of Cu, Zn and Pb. If used as part of the cement raw meal, limited amounts of Cu and Zn can be incorporated into C_3S and C_4AF phases, and after cement hydration Cu and Pb can be bound in C-S-H phases. Also the chemical composition of bottom ash makes it suitable to be used as a corrective agent in raw mix for clinker production. In this study, a clinker was produced with 5% bottom ash as an additive in the raw meal and was characterised for its mineralogy. The early age hydration kinetics were studied using isothermal calorimetry. These measurements show that the properties of clinker with bottom ash as part of the raw meal has comparable properties with that of conventional clinker.

Keywords: Municipal solid waste incineration bottom ash, cement clinker, Alternate fuel and raw materials (AFR), clinker mineralogy, isothermal calorimetry

1. INTRODUCTION

Cement industry being a major contributor to CO_2 emission and energy consumption, it has been focusing on use of alternative fuels and raw materials since long. The main raw materials used are calcareous materials such as limestone which acts as source of calcium, argillaceous materials such as shale, sandstone etc. as source of silica and alumina, ferruginous materials such as iron ore to correct the iron content and other corrective materials to adjust the composition. Using alternative fuels contributes to energy recovery from waste materials and

reduces the need for primary (fossile) energy sources. Exploitation of waste and by-products as alternative raw materials prevents them from going into landfills. The main types of wastes used as alternative fuels include waste oils, tyres, impregnated saw dust, plastic, industrial and household waste, meat and bone meal, agricultural waste, wood chips and other biomass, sewage sludge, refuse derived fuel etc. [3]. Alternative raw materials used include lime sludge from water treatment plants, calcium fluoride, used foundry sand, roasted pyrite, contaminated ore, dusts from steel plants, mill scale, blast furnace slag, fly ash, oil shale, trass, paper residuals, incineration ashes, oil contaminated soil, gypsum from flue gas desulphurisation, ceramic waste etc. The sustainability of each variable considered for production depends on a lot of factors, one of the important ones being transportation of materials. Hence, local solutions have the highest probability to be the most sustainable ones. Municipal solid waste incineration plants are widespread and the residues have a high potential to be used as corrective additions in cement raw meal. The parameters considered while formulating a raw mix and its effects on properties of cement are given below [4].

Lime Saturation Factor (LSF) – This is the ratio of lime (and MgO) present in the mix to the amount of lime required to react with silica, alumina and iron oxide. Excess lime leading to a LSF above 1 leads to higher free lime in the resulting clinker.

$$LSF = \frac{100\ (\ CaO + 0.75\ MgO)}{2.85 SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3} \quad (1)$$

Silica Ratio (SR) – The acceptable value of SR ranges from 1.9 to 3.2. A SR higher than the limit leads to very low burnability of the mix, and also very slow setting and hardening of cement.

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (2)$$

Alumina Ratio – The acceptable value of AR ranges from 1.0 to 4.0. Alumina ratio governs the ratio of aluminate to ferrite phases, and the liquid formed. The quantity of liquid formed is maximum at AR of 1.38. [4]

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad (3)$$

Hydraulic Modulus (HM) - The prescribed value of hydraulic modulus is between 1.7 and 2.3. Mixes with higher HM show poor volume stability and those with lower HM show poor strength.

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \quad (4)$$

Cement is produced by sintering raw meal to approximately 1450^{o}C. The main phases of cement formed are alite, belite, aluminate and ferrite.

Based on the point of collection, the residues from incineration plants are classified as bottom ash, boiler ash and fly ash, out of which bottom ash constitutes about 85% of whole residue. The composition of bottom ash is specific to the size fraction. The ash used in this study was collected from grate furnace installation of Indaver in Doel, Belgium. The residues are sorted into different size fractions, >50mm, 6-50mm, 2-6mm and 0-2 mm. The fraction of bottom ash

between sizes 0 and 2 mm is used in this study and has the highest organic carbon content out of different bottom ash fractions from the incinerator. That makes it unsuitable to be used as supplementary cementitious material in cement. Another characteristic that makes it unsuitable is the presence of heavy metals such as Cu, Zn and Pb. Limited quantities of these heavy metals can be incorporated into cement phases. Presence of Cu above a threshold of 0.35% has the effect of decomposition of alite to belite and free lime [5]. Zn can be fixed in C_3S, C_3A and C_4AF. Its content up to 1% does not affect the stability of clinker phases. However, increased Zn content above a threshold of 0.7% causes retardation of hydration [6]. Further, Cu and Pb is fixed in C-S-H, the main phase in hydrated cement [7]. In this study, 0-2 mm fraction of bottom ash is used as a corrective agent in raw mix for clinker production, which is identified as the best method to valorize this fraction.

2. MATERIALS AND METHODS

The raw materials used for making raw meal were limestone, shale, two types of bauxite, overburden and bottom ash. For the bottom ash, the 0-2 mm fraction was used as a corrective agent and constituted 5% of the cement raw meal. The chemical composition of all the raw materials were determined by XRF. The milled raw materials were proportioned, and mixed into a slurry, which was then dried into pellets of 5 mm size. These pellets were sintered in a platinum crucible in a bottom loading furnace up to a temperature of 1500^{o}C with a residence time of one hour, and then quenched by exposing suddenly in air to prevent alite decomposing back to belite and lime. The chemical composition of the raw materials and the percentage of each in the raw meal is shown in Table 1. The values of all the parameters for the raw mix used, raw meal-BA in present study are shown in Table 2.

Table 1 Chemical composition of raw mix, constituents and control CEM I 52.5N

Raw material	Lime stone	Shale	Bauxite 1	Bauxite 2	Overburden	BA 0/2	Raw meal BA	CEM I 52.5N Commercial cement
%	80.50	1.00	1.00	1.50	11.00	5.00	100.00	-
Ca	50.16	1.71	0.79	4.51	5.06	16.50	41.85	63.00
Si	3.88	51.92	28.34	4.68	64.79	41.44	13.20	21.40
Al	0.78	20.67	27.44	50.93	10.62	9.39	3.51	5.00
Fe	0.68	8.25	21.73	21.21	4.52	10.17	2.17	2.46
Mg	1.53	1.97	0.99	0.26	1.94	1.41	1.55	2.17
Na	0.06	0.73	0.14		1.00	2.78	0.31	
K	0.12	3.42	0.05	0.15	2.14	1.61	0.45	0.41
S	0.06	0.93		0.37	0.06	1.75	0.16	4.64

Table 2 Parameters of raw mix (raw meal – BA)

LSF	1.00
SR	2.32
AR	1.62
HM	2.22

The clinker was ground in isopropanol medium and dried in air. Then, the ground clinker was mixed with zincite as internal standard and mineralogical examination was carried out with a thermo-scientific diffractometer with Cu-Kα radiation, angular scan 5-70^{o}C with a step size of 0.02, and the constituents were quantified by Rietveld analysis. The clinker was mixed with 3% gypsum and the resulting cement was mixed with water at a w/c ratio of 0.5. The heat of hydration of the cement paste was measured in a TAM Air isothermal calorimeter at 20^{o}C.

3. RESULTS AND DISCUSSIONS

Table 3 shows the cement phase composition in commercial CEM I 52.5N and in the laboratory mix CEM I - BA. The laboratory preparation of clinker with BA0/2 yielded higher alite and aluminate. It is difficult to make a real evaluation of the reasons, since the raw mix composition of the commercial cement is unknown. Figure 1 shows the hydration kinetics of cement from the laboratory mix CEM I –BA compared to commercial cement CEM I 52.5N. Presence of anhydrite content in commercial cement is due to the high temperature during grinding. In the laboratory mix, sulphate was added in form of gypsum and mixed by hand. In presence of anhydrite, early hydration of C_3A is lower. This, combined with higher aluminate content in the lab mix CEM I – BA may have resulted in the lower heat release during the induction period for commercial cement [8]. Figure 2 shows cumulative heat of hydration of both cements under study. The laboratory mix CEM I – BA shows a higher cumulative heat release. This can be attributed to higher alite and aluminate contents.

Table 3 Phase composition of commercial cement CEM I 52.5N and laboratory mix CEM I – BA

	CEM I 52.5N	CEM I - BA
Alite	51.6	57.1
Belite	20.8	13.8
Aluminate	3.4	5.3
Ferrite	8.2	9.3
Gypsum	2.5	3
Anhydrite	2.1	-
Amorphous / Undetected	10.6	11.3

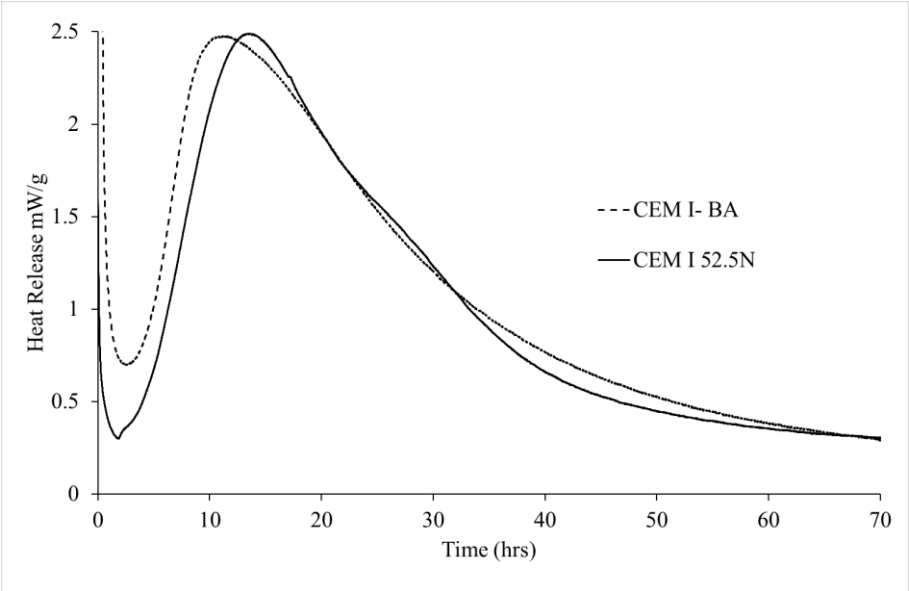

Figure 1 Heat of hydration of commercial cement CEM I 52.5N and CEM I – BA made in the laboratory

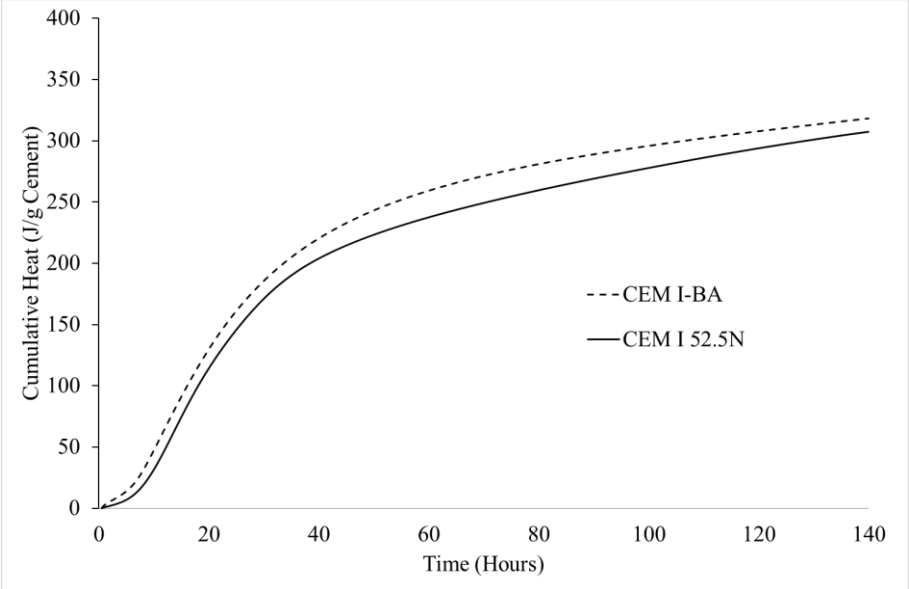

Figure 2 Cumulative heat of hydration of commercial cement CEM I 52.5N and clinker CEM I – BA made in the laboratory

11. CONCLUSIONS

- Municipal solid waste incineration ash can be effectively used as a corrective additive in the raw mix for clinker production.
- Clinker produced by replacement of 5% of raw meal generated clinker with comparable mineralogy and hydration kinetics as that of commercial cement.

- The higher cumulative heat of hydration measured for the laboratory cement made from the raw meal with bottom ash can be attributed to higher alite and aluminate content in the laboratory cement CEM I – BA.
- Higher heat release during the induction period for the lab cement CEM I – BA in comparison with the commercial cement could be attributed to the combined effect of lower C_3A content and higher anhydrite content in the commercial cement.

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